

## PATENT ABSTRACTS OF JAPAN

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(71)Applicant : SEKISUI CHEM CO LTD

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(72)Inventor : IUCHI KENJI

TONO MASAKI

IWANE KAZUYOSHI

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### (54) FLAME-RETARDANT THERMOPLASTIC RESIN COMPOSITION

#### (57)Abstract:

PURPOSE: To obtain a flame-retardant thermoplastic resin composition made highly flame-retardant without using any halogen compound and giving a molding not deteriorating in mechanical properties by mixing a thermoplastic resin with a heat-expansible graphite and a boron compound.

CONSTITUTION: This flame-retardant thermoplastic resin composition comprises 100 pts.wt. thermoplastic resin and 5-150 pts. wt. mixture comprising a heat- expansible graphite and a boron compound. This composition may further contain an inorganic oxide as a flame-retardant aid. Examples of the inorganic oxides used include magnesium oxide, manganese oxide, silicon oxide, iron oxides, cobalt oxide, nickel oxide, aluminum oxide, zinc oxide, titanium oxide and tin oxide. These oxides may be used alone or in the form of a mixture of at least two oxides. These oxides have a function of lowering the decomposition temperature of a metal borate close to that of the thermoplastic resin and to thereby improve the flame retardancy of the resin.

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CLAIMS

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[Claim(s)]

[Claim 1] The fire-resistant thermoplastics constituent characterized by consisting of mixture 5 of the thermoplastics 100 weight section, a thermal-expansion nature graphite, and a boron content compound - the 150 weight sections.

[Claim 2] The fire-resistant thermoplastics constituent characterized by an inorganic oxide 0.1 - 30 weight sections being further added by the fire-resistant thermoplastics constituent of claim 1.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to a fire-resistant thermoplastics constituent.

[0002]

[Description of the Prior Art] Although thermoplastics generally has many which are easy to burn, since fire-resistant grant is strongly demanded with expansion of an application in recent years, flameproofing processing is performed by various approaches. For example, in order to give fire retardancy to polyolefine system resin, generally the approach of adding a halogen content compound is performed. Although it was possible surely to have given advanced fire retardancy, in order for there to be corrosion of a surrounding device since there is a possibility of generating corrosive gas, at the time of fabrication and combustion, and to process corrosive gas, the special facility was required of this approach.

[0003] As an approach of giving fire retardancy, without using a halogen content compound, the approach using the hydration metallic oxide which does not generate a toxic gas at the time of combustion of an aluminum hydroxide, a magnesium hydroxide, basic magnesium carbonate, etc. is indicated by JP,57-165437,A and JP,61-36343,A. However, in order to give sufficient fire retardancy for the thermoplastics which is easy to burn using the above-mentioned hydration metallic oxide, a lot of hydration metallic oxides needed to be added, and the mold goods obtained had the trouble that the fall of a mechanical strength was remarkable and could not present practical use.

[0004] Moreover, although the approach of giving fire retardancy to JP,58-67737,A to polyolefine system resin by using together the hydrate, red phosphorus system flame retarder, and thermal-expansion nature graphite of inorganic metallic compounds, for example was indicated, since red phosphorus was the dangerous substance, it is difficult handling and had the trouble that a mechanical property fell remarkably, by the approach to add the hydrate of inorganic metallic compounds.

[0005] Furthermore, although the method of using a thermal-expansion nature graphite as a flame retarder independently was indicated by JP,3-41163,A and JP,3-41164,A for example, in order to acquire high fire retardancy, it is necessary to add upwards so much, the thermal-expansion nature graphite expanded at the time of combustion, and there was also a trouble that a lot of graphites dispersed.

[0006]

[Problem(s) to be Solved by the Invention] It is in providing the Plastic solid which the purpose can give the fire retardancy which was excellent, without using a halogen content compound by having not made this invention in view of the above-mentioned fault, and is acquired with the fire-resistant thermoplastics constituent with which the fall of a mechanical property does not take place.

[0007]

[Means for Solving the Problem] The fire-resistant thermoplastics constituent of this invention consists of mixture of thermoplastics, a thermal-expansion nature graphite, and a boron content compound.

[0008] Especially the thermoplastics used by this invention is not limited, and a polypropylene resin, polyethylene system resin, Pori (1-butene) system resin, poly pentene system resin, polystyrene system resin, ABS (acrylonitrile-styrene butadiene rubber) system resin, polycarbonate system resin, polyphenylene ether system resin, polyamide system resin, acrylic resin, etc. are mentioned.

[0009] As the above-mentioned polypropylene resin, any of a propylene homopolymer (polypropylene), the copolymers which use a propylene as a principal component, or such mixture are sufficient, and the propylene-alpha olefin copolymer which uses a propylene as a principal component can be mentioned as a copolymer which uses a propylene as a principal component, for example. As the above-mentioned alpha olefin, ethylene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-butene, 1-pentene, etc. are mentioned,

for example.

[0010] As the above-mentioned polyethylene system resin, any of an ethylene homopolymer (polyethylene), the copolymers which use ethylene as a principal component, or such mixture are sufficient, as a copolymer which uses ethylene as a principal component, the ethylene-alpha olefin copolymer which uses ethylene as a principal component can be mentioned, for example, and a propylene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-butene, 1-pentene, etc. are mentioned as an alpha olefin, for example.

[0011] As copolymers other than the above-mentioned alpha olefin, an ethylene-vinylacetate copolymer, an ethylene-ethyl (meta) acrylate copolymer, an ethylene-methyl (meta) acrylate copolymer, etc. are mentioned.

[0012] The blend mold polymer of the copolymers which use acrylonitrile, a butadiene, and styrene as a principal component as the above-mentioned ABS (acrylonitrile-styrene butadiene rubber) system resin, for example and these polymer blend object; styrene acrylonitrile copolymers, and acrylonitrile-butadiene copolymerization rubber; the graft mold polymer obtained by carrying out the graft copolymerization of styrene and the acrylonitrile is listed to the bottom of coexistence of a butadiene rubber latex or styrene-butadiene-rubber RATTEKUSU.

[0013] as the above-mentioned polystyrene system resin -- homopolymer [ of vinyl aromatic compound monomers, such as nuclear substitution styrene of alpha-permutation styrene monomers, such as styrene and alpha methyl styrene, such as homopolymer; vinyltoluene, ]; -- the graft copolymer to which the graft of the copolymer of these monomers and these monomers, and other copolymerizable monomers or these was carried out is mentioned.

[0014] A having maintained the layer structure's of carbon which well-known matter's could be conventionally used [ carbon ] as thermal-expansion nature graphite used by this invention, for example, powder's, such as natural scale-like graphite, pyrolysis graphite, and kish graphite's, was processed [ carbon ] with oxidants, such as inorganic-acids [ , such as concentrated sulfuric acid, a nitric acid, and a selenic acid, ], concentrated-nitric-acid, perchloric acid, perchlorate, permanganate, dichromate, and hydrogen peroxide's, and made intercalated graphite's generate crystal compound is mentioned.

[0015] After acid treatment of the above-mentioned thermal-expansion nature graphite is carried out, further Ammonia, an aliphatic series low-grade amine, What was neutralized with the alkali metal compound, the alkaline-earth-metal compound, etc. is desirable. As the above-mentioned aliphatic series low-grade amine For example, monomethylamine, dimethylamine, a trimethylamine, ethylamine, Propylamine, a butylamine, etc. are mentioned and hydroxides, such as a potassium, sodium, calcium, barium, and magnesium, an oxide, a carbonate, a sulfate, an organic-acid salt, etc. are mentioned as the above-mentioned alkali metal compound and an alkaline earth metal compound.

[0016] When the dilatation of a thermal-expansion nature graphite will become small, the fire retardancy of the mold goods obtained as a result will fall, if it becomes small, and the grain size of the above-mentioned thermal-expansion nature graphite becomes large, its dispersibility at the time of mixing [ thermoplastics and ] and kneading is bad, and since the physical properties of the mold goods obtained fall, 20-200 meshes are desirable [ grain size ].

[0017] As a boron content compound used by this invention, a metal borate is mentioned, for example. A metal borate is the generic name of the oxo-salt of a boric acid, for example, when M is used as the metal of monovalence, it is a compound expressed with general formula  $xM_2O \cdot yB_2O_3 \cdot zH_2O$  (x and y show the natural number among a formula, and z shows zero or more integers). As a metal shown by M, sodium, a potassium, magnesium, calcium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, aluminum, etc. are mentioned. In the above-mentioned metal borate, especially, boric-acid zinc and manganese borate are desirable, and a borosilicate, borane (however, what is stable in air), a metal HOU compound, etc. are suitably used in addition to this. Even if the above-mentioned boron content compound is used independently, two or more sorts may be used

together.

[0018] As mixture of the above-mentioned thermal-expansion nature graphite and a boron content compound, that with which a thermal-expansion nature graphite and a boron content compound are mixed by the weight ratios 1:9-9:1 is desirable, and are the weight ratios 1:3-3:1 more preferably. In the above-mentioned mixture, since the ratio of a thermal-expansion nature graphite will fall if sufficient fire-resistant effectiveness is not acquired and the rate of a boron content compound increases, since the graphite which expanded at the time of combustion will disperse, if the rate of a thermal-expansion nature graphite increases, sufficient fire-resistant effectiveness is not acquired and cuts.

[0019] In the resin constituent of this invention, since sufficient fire retardancy will no longer be acquired if the mechanical strength of the mold goods which will be obtained if it increases falls and decreases, the amount of the above-mentioned mixture used is the 5 - 150 weight section to the thermoplastics 100 weight section.

[0020] Phosphorus compounds may be blended with the resin constituent of this invention. As the above-mentioned phosphorus compounds, for example Triphenyl phosphate, tricresyl phosphate, Phosphoric ester, such as octyl diphenyl phosphate and trixylenyl phosphate; Phenylphosphonic acid, Phosphonic acid, such as isopropyl phosphonic acid, n-butyl phosphonic acid, and t-butyl phosphonic acid; Sodium phosphate, Ammonium phosphate besides the hydrate of phosphoric-acid metal salts, such as potassium phosphate, magnesium phosphate, calcium phosphate, and phosphoric-acid zinc, and those metal salts, ammonium polyphosphate, red phosphorus, etc. are mentioned, and even if these are used independently, two or more sorts may be used together. Use of ammonium polyphosphate is desirable from compatibility with resin, or the ease of handling especially among the above-mentioned phosphorus compounds.

[0021] In order to prevent autogenous ignition at the time of adding and kneading to moisture resistance and resin as the above-mentioned red phosphorus, that by which the front face of a red phosphorus particle was covered with resin is desirable.

[0022] An inorganic oxide may be further added as a fire-resistant assistant by the fire-resistant thermoplastics constituent of this invention. As an inorganic oxide, magnesium oxide, manganese oxide, oxidization silicon, ferrous oxide, cobalt oxide, nickel oxide, an aluminum oxide, a zinc oxide, titanium oxide, tin oxide, etc. are mentioned, and even if these are used independently, two or more sorts may be used together, for example. These inorganic oxides reduce the decomposition temperature of a metal borate, are brought close to the decomposition temperature of thermoplastics, and raise fire retardancy.

[0023] The amount of the above-mentioned inorganic oxide used has desirable 0.1 - 30 weight section to the thermoplastics 100 weight section.

[0024] Furthermore, antioxidants, such as a phenol system, an amine system, and a sulfur system, a metal damage inhibitor, a bulking agent, an antistatic agent, a stabilizer, a cross linking agent, lubricant, a softener, a pigment, etc. may be added by the fire-resistant thermoplastics constituent of this invention in the range which does not spoil the physical properties of a constituent.

[0025] Mold goods are obtained by \*\* which the above-mentioned fire-resistant thermoplastics constituent carries out melting kneading for example, of each component using kneading equipments, such as a single screw extruder, a twin screw extruder, a Banbury mixer, a kneader mixer, and a roll, and carries out fabrication to the shape of a sheet, tabular, etc.

[0026]

[Example] Next, the example of this invention is explained.

[0027] (Examples 1-6, examples 1-6 of a comparison) According to the molding temperature which shows the thermoplastics, the thermal-expansion nature graphite, the boric-acid zinc, ammonium polyphosphate, and titanium oxide of the specified quantity shown in Tables 1 and 2 in Tables 1 and 2, melting kneading was carried out using the lab PURASUTO mill, and the fire-resistant thermoplastics constituent was obtained. Press forming of the obtained resin constituent was carried out with the

molding temperature indicated to Tables 1 and 2, and the object for oxygen-index measurement and the sample for tension tests were produced, respectively.

[0028] In addition, front Naka and the following component were used.

- Polypropylene : consistency =0.90 (g/cm<sup>3</sup>), MI=1.5 (g / 10 minutes)

It was displayed as front Naka PP.

- Low density polyethylene : consistency =0.92 (g/cm<sup>3</sup>), MI=3.4 (g / 10 minutes)

It was displayed as front Naka LDPE.

- Ethylene-vinylacetate copolymer vinyl acetate content = it was displayed as consistency =0.92(g/cm<sup>3</sup>) MI=2.5 (g / 10 minutes) and front Naka EVA 19% of the weight.

- Acrylonitrile-butadiene-styrene copolymer : consistency =1.20 (g/cm<sup>3</sup>), MI=22 (g / 10 minutes)

It was displayed as front Naka ABS.

- Polystyrene : consistency =1.06 (g/cm<sup>3</sup>), MI=1.7 (g / 10 minutes)

It was displayed as front Naka PSt.

- Thermal-expansion nature graphite : "CA-60S" by Nippon Kasei Chemical Co., Ltd.

- Boric-acid zinc : the product made from Borax "2233"

- Ammonium polyphosphate : "Sumisafe P" by Sumitomo Chemical Co., Ltd.

- Titanium oxide : Ishihara Sangyo Kaisha, Ltd. make (a rutile mold, particle size of 5 micrometers or less)

[0029] The following evaluation was performed using the test piece obtained in the above-mentioned example and the example of a comparison, and the result was shown in Tables 1 and 2.

(1) Fire-resistant sex test JIS Based on K7201, the No. A-1 test piece (3.0mm in die length of 150mm, width of face of 6.5mm, thickness) was cut down from the above-mentioned oxygen-index test sample, the oxygen index was measured, and fire retardancy was judged on the following criteria.

O : -- an oxygen index -- 30 or more thing O: -- an oxygen index -- or more 28 less than 30 thing x: -- the oxygen index made x less than 28 thing, in addition the thing to which the graphite which expanded disperses during oxygen-index measurement, and made O what not dispersing.

[0030] (2) Tractive characteristics JIS The tension test was performed based on K7113, and O and less than 200% of thing were made into x for the thing of 200% or more of elongation percentages.

[0031]

[Table 1]

		実 施 例					
		1	2	3	4	5	6
難燃性熱可塑性樹脂組成物 (重量部)	PP	100	—	—	—	50	—
	LDPE	—	100	—	—	15	—
	EVA	—	—	—	—	35	100
	ABS	—	—	—	100	—	—
	PS t	—	—	100	—	—	—
	熱膨張性黒鉛	4	40	20	30	20	90
	ホウ酸亜鉛	4	25	60	15	120	15
	ポリリン酸 アンモニウム	2	—	3	10	—	3
	酸化チタン	2	3	3	—	—	—
成形温度 (°C)		170	170	170	180	170	170
難燃性	酸素指数	○	◎	◎	○	◎	◎
	黒鉛の飛散	○	○	○	○	○	○
引張特性		○	○	○	○	○	○

[0032]

[Table 2]

		比 較 例					
		1	2	3	4	5	6
難燃性熱可塑性樹脂組成物 (重量部)	PP	100	—	—	50	70	—
	LDPE	—	100	—	50	—	—
	EVA	—	—	—	—	30	—
	ABS	—	—	100	—	—	—
	PS t	—	—	—	—	—	100
	熱膨張性黒鉛	3	—	2	40	4	150
	ホウ酸亜鉛	—	30	2	—	0.1	50
	ポリリン酸 アンモニウム	—	10	—	—	—	—
	酸化チタン	—	—	—	—	250	—
成形温度 (°C)		170	170	180	170	170	170
難燃性	酸素指数	×	×	×	○	○	※
	黒鉛の飛散	×	—	○	×	×	※
引張特性		○	○	○	○	×	※

※：脆性のため試験片作製できず

[0033]

[Effect of the Invention] It is as above-mentioned, and since there is also no generating of halogen system gas at the time of combustion and processing and there is also no scattering of an expansibility graphite at the time of combustion, the fire-resistant thermoplastics constituent of this invention is usable for a broad application, while it has the outstanding fire retardancy.

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[Translation done.]